1995

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Publication Info

Journal of the Electrochemical Society, 1995, pages 154-156.

http://www.electrochem.org/
DOI: 10.1149/1.2043855
Publisher's link: http://dx.doi.org/10.1149/1.2043855

Hydrogen-Atom Direct-Entry Mechanism into Metal Membranes

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ABSTRACT

The hydrogen-atom direct-entry mechanism is used to explain why the steady-state hydrogen permeation current density through a metal membrane is directly proportional to the cathodic current density, i_c, and is independent of the membrane thickness when i_c is small.

Bagotskaya[1] and later Frumkin[2] postulated that hydrogen atoms enter directly into a metal membrane and do not go through an intermediate adsorbed state. The mechanism they proposed is

$$H^+ + M + e^- \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} MH_{abs} \quad [1]$$

$$H^+ + M + e^- \overset{k_2}{\rightarrow} MH_{ads} \overset{k_3}{\rightarrow} \frac{1}{2}H_2 + M \quad [2]$$

where k_1, k_{-1}, k_2, and k_3 are rate constants.

Bockris *et al.*[3] checked this mechanism by considering the following equations

$$J_\infty = F\left[k_1\left(1 - \frac{C_o}{C_s}\right)e^{-\alpha_1 a\eta} - k_{-1}C_o e^{(1-\alpha_1)a\eta}\right] \quad [3]$$

$$i_c = i_o e^{-\alpha_2 a\eta} \quad [4]$$

$$j_\infty = \frac{DF}{L}C_o \quad [5]$$

where j_∞ is the steady-state permeation current density, η is the overpotential, $a = F/RT$, C_o is the hydrogen concentration directly beneath the cathode surface, C_s is the saturation value of C_o, α_1 is the transfer coefficient of reaction 1, α_2 is the transfer coefficient of reaction 2, i_c is the cathodic current density, D is the hydrogen diffusion coefficient, and L is the membrane thickness. Bockris *et al.*[3] used Eq. 3 to 5 to claim that the hydrogen permeation current density is proportional to the cathodic current density squared

$$j_\infty \propto i_c^2 \quad [6]$$

Since no experimental evidence exists in literature to support Eq. 6, Bockris *et al.*[3] concluded that the direct entry mechanism does not predict the observed results and is unable to explain the hydrogen permeation through a membrane.

The hydrogen atom direct mechanism[1,2] is used here to explain why the steady-state hydrogen permeation current density (j_∞) is directly proportional to the cathodic current density (i_c) and is independent of the membrane thickness when i_c is small. Assuming that the metal is far from saturation, then $1 - C_o/C_s \approx 1$, and if in reaction 1, k_{-1} is negligible to k_1, Eq. 3 becomes

$$j_\infty = Fk_1 e^{-\alpha_1 a\eta} \quad [7]$$

The ratio of Eq. 7 to 4 is

$$\frac{j_\infty}{i_c} = \frac{Fk_1 e^{-\alpha_1 a\eta}}{i_o e^{-\alpha_2 a\eta}} \quad [8]$$

and assuming that the overpotential for the electrode (η) aplies to both reactions 1 and 2

$$j_\infty = i_c \frac{Fk_1}{i_o} e^{-(\alpha_2 - \alpha_2)a\eta} \quad [9]$$

If $\alpha_1 = \alpha_2$, Eq. 9 shows that j_∞ is directly proportional to i_c, which is in agreement with previous experiment work[4-9] that was done under conditions consistent with the development of Eq. 9. For example, Early[4] reported that j_∞ through palladium membranes is directly proportional to i_c when i_c is less than 200 $\mu A/cm^2$. Heath[5] reported the same for i_c less than 22 mA/cm^2. Raczynski[6] and Zacrozymski *et al.*[7] demonstrated that $j_\infty \propto i_c$ for low values of i_c for hydrogen permeation through iron. Also Evseev[8] reported that $j_\infty \propto i_c$ for iron for values of i_c between 5 and 80 mA/cm^2.

Note that Eq. 9 shows that j_∞ does not depend on the thickness of the metal membrane (L). This is consistent with results presented by Hoare and Schuldiner[9,10] and Bowker and Piercy[11] for Pd membranes.

Experimental

The Devanathan-Stachurski permeation technique[12] was used to investigate the rate of hydrogen permeation through a HY-130 steel and through palladium membranes with an area of approximately 4 cm^2 with thicknesses of 0.15 and 0.025 mm, respectively. The permeation experiments were carried out in a system with two compartments, separated by a bipolar membrane made of HY-130 steel or palladium.

The electrolyte on the cathodic side of the cell for the HY-130 steel membranes was $1M$ Na_2SO_4, $0.4M$ NaCl, and $1M$ H_3BO_3 and for the palladium membrane was $1N$ H_2SO_4. Atomic hydrogen permeation transients through a HY-130 steel membrane for different applied cathodic potentials were recorded continuously as a function of time. At the beginning of each experiment, the cathodic side of the steel membrane was held at a constant potential of -0.58 V *vs.* SCE. Next, the potential was stepped to a more negative value after the hydrogen permeation current density reached a steady-state value. After the permeation stabilized at an applied potential of about -0.87 V *vs.* SCE, the potential was switched off, and a decay curve was recorded. The palladium alloy membrane on the cathodic side of the cell was polarized galvanostatically using a low cathodic current density in the range of 59.4 to 594.3 $\mu A/cm^2$.

The electrolyte on the anodic side of the cell for a HY-130 steel membrane was $0.2M$ NaOH while for the palladium membrane it was $1N$ H_2SO_4. To avoid passivation or dissolution, the anodic side of the HY-130 membrane was electroplated with a thin layer (0.15 to 0.20 μm) of palladium. The electrodeposition of palladium was carried out in an electrolyte containing $2 \times 10^{-5}M$ $Na_2Pd(NO_2)_4$ using a current density of 100 $\mu A/cm^2$ for 2 h. After the electrolyte was drained off, the compartment was washed with deionized water and filled with the anodic solution.

The potential on the anodic side for HY-130 steel membranes (the side from which the hydrogen emerges) was set at -0.3 V *vs.* a Hg/HgO reference electrode placed in the solution in the cell. The permeation rate through a palladium membrane was measured by setting the potential at a fixed value of 0.3 V *vs.* a SCE. These values of the set potentials correspond to a practically zero concentration of absorbed atomic hydrogen on the anodic surface of the mem-

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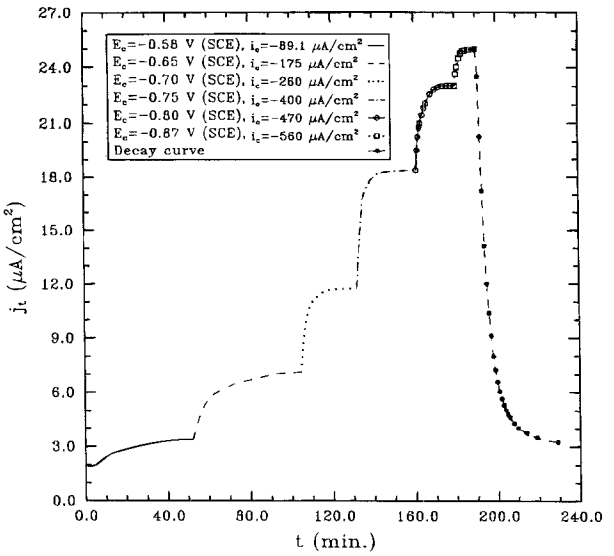

Fig. 1. Atomic hydrogen permeation transients through a HY-130 steel membrane as a function of time for different applied cathodic potentials in a catholyte containing 1*M* Na_2SO_4, 0.4*M* NaCl, and 1*M* H_3BO_3. The thickness of the membrane was *L* = 0.15 mm.

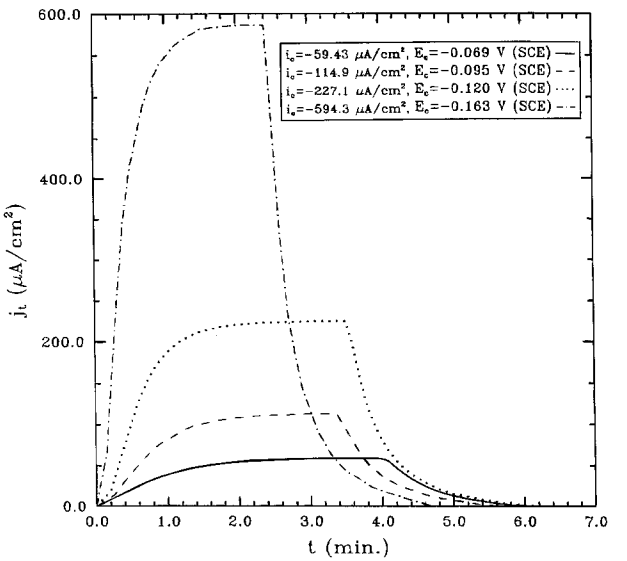

Fig. 3. Hydrogen permeation transients through a Pd membrane obtained at constant cathodic current densities. The thickness of the palladium membrane was *L* = 25 μm. The catholyte was 1*N* H_2SO_4.

brane. Prepurified nitrogen was bubbled through both compartments in order to keep them free from oxygen contamination.

Results and Discussion

Atomic hydrogen permeation transients through a HY-130 steel membrane as a function of time for different applied potentials are shown in Fig. 1. The plateaux in Fig. 1 represent the j_∞ values for different values of E_c. The corresponding cathodic current density, i_c, was recorded for each value of E_c. As expected, the permeation current densities increased as the applied cathodic potentials and the resulting cathodic current densities were increased. Figure 2, a plot of j_∞ *vs.* i_c, is clearly linear.

Permeation transients through a palladium membrane were obtained as a function of applied cathodic current densities, as shown in Fig. 3. The plateaux in Fig. 3 represent j_∞ values for the associated set of i_c values. The permeation current density, j_∞, for palladium also increases linearly with the cathodic current density, as shown in Fig. 4.

Conclusion

The direct hydrogen entry mechanism[1,2] was shown to be correct for HY-130 steel and Pd for small values of j_c. A simple expression (Eq. 9) was developed that showed that the hydrogen permeation current density, j_∞, is directly proportional to the applied cathodic current density, i_c, and is independent of the thickness of the metal membrane. This expression was shown to be consistent with experimental data presented here and with data from previous workers.

Acknowledgment

Technical assistance and financial support by A. John Sedriks, the Office of Naval Research, under Contracts No. N00014-93-1-0259 and AASERT N00014-93-1-1094 are gratefully acknowledged.

Manuscript submitted Nov. 15, 1993; revised manuscript received Sept. 19, 1994.

The University of South Carolina assisted in meeting the publication costs of this article.

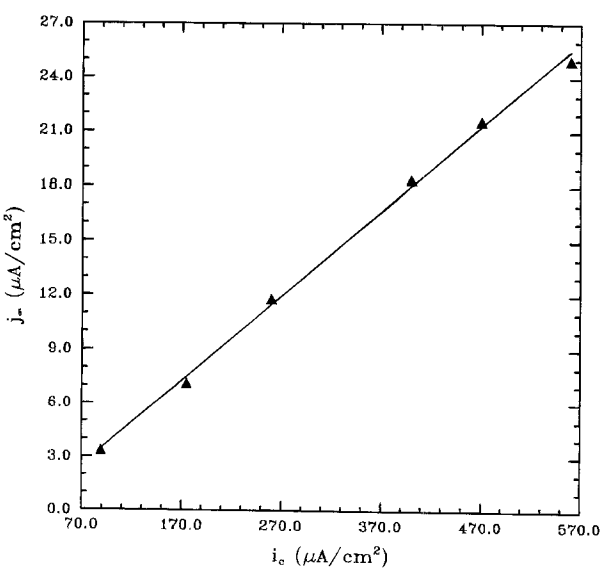

Fig. 2. The steady-state hydrogen permeation current density (j_∞) as a function of the cathodic current density (i_c) through the HY-130 steel membrane.

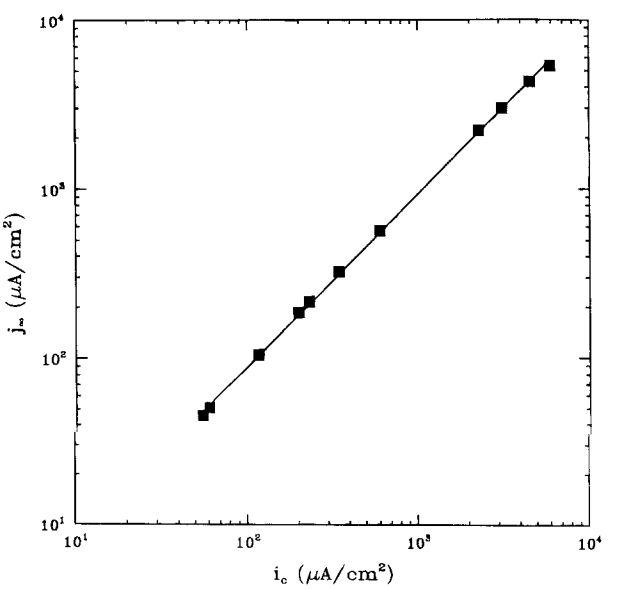

Fig. 4. The steady-state hydrogen permeation current density (j_∞) as a function of the cathodic current density (i_c) through a palladium membrane (*L* = 25 μm).

LIST OF SYMBOLS

a	F/RT, V^{-1}
C_o	hydrogen concentration directly beneath the cathode surface, mol cm^{-3}
C_s	saturation value of C_o, mol cm^{-3}
D	hydrogen diffusivity, $cm^2\ s^{-1}$
E_c	cathodic potential, V
F	Faraday's constant, 96,487 C $(eq)^{-1}$
i_c	cathodic current density, A cm^{-2}
i_o	exchange current density, A cm^{-2}
j_∞	steady-state hydrogen permeation current density, A cm^{-2}
k_1	absorption constant, mol $(cm^2\ s)^{-1}$
k_{-1}	desorption constant, cm s^{-1}
k_3	hydrogen recombination rate constant, mol $(cm^2\ s)^{-1}$
L	membrane thickness, cm
R	gas constant, 8.3143 J$(mol\ K)^{-1}$
T	temperature, K

Greek

α_1, α_2	transfer coefficients, dimensionless
η	overpotential, V

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